

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
20 November 2003 (20.11.2003)

PCT

(10) International Publication Number
WO 03/095078 A1

(51) International Patent Classification⁷: B01D 65/06,
65/02, C12H 1/06, B01D 41/04

(21) International Application Number: PCT/NL03/00461

(22) International Filing Date: 23 June 2003 (23.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
02077580.5 28 June 2002 (28.06.2002) EP

(71) Applicant (for all designated States except US): NED-ERLANDSE ORGANISATIE VOOR [NL/NL];
Toegepast-Natuurwetenschappelijk Onderzoek TNO,
Schoemakerstraat 97, NL-2628 VK Delft (NL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): JETTEN, Jan, Matthijs [NL/NL]; Costerlaan 36, NL-3701 JL Zeist (NL). SLAGHEK, Theodoor, Maximiliaan [NL/NL]; Schansweg 35, NL-3042 HT Rotterdam (NL).

(74) Agent: VAN WESTENBRUGGE, Andries et al; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- upon request of the applicant, before the expiration of the time limit referred to in Article 21(2)(a)

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/095078 A1

(54) Title: PROCESS FOR CLEANING FILTERS

(57) Abstract: Filters used in the beverage industry fouled by polyphenol-protein complexes and carbohydrate polymers can be cleaned by treating the filters either with the following methods: -Solubilisation of at least part of the carbohydrate polymers followed by a treatment of the resulting polyphenol protein complex with an oxidative chemical. -Treatment of the fouled filters through a back-wash method using an oxidative chemical. In both cases it is not necessary to rinse the membranes after cleaning with a reductive chemical.

Process for cleaning filters

The invention relates to a process of cleaning food processing equipment, in particular membrane filters which are used for producing liquid foodstuffs, wherein the filters are contacted with an oxidator.

5 In the food industry, use is being made to an increasing extent of membrane filters, in particular plastic membranes such as polyvinylpyrrolidone, polysulphone, polyether-sulphone and certain types of polyamides, and ceramic membranes for removing undesirable insoluble matter from beverages and other liquids. Such membranes are also used for cleaning surface water. Such membranes ensure an
10 expedient removal of undesirable constituents, in particular micro-organisms such as algae, fungi, yeast, and bacteria.

The problem is, however, that such membrane filters become blocked even after a short time so that they become unusable. The blocked filters can be regenerated, for example by rinsing them through in the opposite direction. However, that is a
15 complicated process and no longer effective in the long term because the contamination accumulates. In addition, it is difficult to remove some persistent organic contaminants in this way.

Enzymatic processes have been proposed for cleaning membranes. Thus, WO 98/45029 describes the use of cellulases and amylases for cleaning beer filtering
20 membranes, after alkaline pretreatment of the membrane. Similarly, JP-A 4-267933 describes the use of proteinases and cellulases for cleaning separation membranes. These non-oxidative processes, however, are usually insufficiently effective in cleaning blocked membranes.

WO 97/45523 describes the use of 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) as nitroxyl compound and hypochlorite and hypobromite as a reoxidator for cleaning beer-settling modules. The presence of halogen residues, especially bromine residues, is highly undesired in equipment used for preparing or treating beverages and other foodstuffs. Moreover, the amounts of oxidator and reoxidator used are high and therefore this method is relatively expensive.

WO 99/15256 discloses the use of cyclic nitroxyl compounds such as TEMPO together with a calcium-sequestering agent for cleaning filters to be used in purifying surface water. This method is not very effective for cleaning filters with heavy residues produced in the beverage industry.

5 US 5,647,988 and JP-A 9-290141 disclose a method for cleaning ceramic membranes used in water-purification plants and the like, by using a back-washing method in combination with an oxidising agent such as sodium hypochlorite, chlorine and chlorine dioxide followed by a washing with a reducing agent.

10 Research has revealed that during the membrane separation process for cleaning foodstuffs such as beer, the membrane fouling starts with a complexation onto the membrane consisting of a complex of polyphenols and proteins. Subsequently other components such as (poly)saccharides and/or other hydrophilic residues of e.g. yeast adsorb onto the polyphenol protein complex and as a result the pores of the membranes are blocked. The blocking of the membrane pores results in reduced permeability and 15 ultimately in an inefficient filtration process.

20 In order to clean the used membranes, it was surprisingly found that filters and other equipment used in the food and beverage industry can be effectively cleaned in a TEMPO-free process. The cleaning process is focused on targeting the polyphenol protein complex with an oxidising chemical aid such as sodium hypochlorite, Oxone, organic peracids or a transition metal complex together with peroxide compounds such 25 as hydrogen peroxide or with hypohalous acids. In all cases it is not necessary that after the oxidative cleaning the membranes are treated with a reducing agent. The research has resulted in two embodiments, which are feasible for cleaning the membranes. The two embodiments of the method of the invention have in common, as the inventive concept, that the protein and/or polyphenol-containing residues are treated with the oxidising agent capable of oxidising the proteins and/or polyphenols, while minimising contact of the oxidising agent with the polysaccharides. The reduced contact with oxidising agent has the further advantage that the life cycle of the membranes is increased.

30 The first embodiment is focused on a two-step circular cleaning sequence whereby first the carbohydrates or other hydrophilic residues, which are attached onto the polyphenol protein complex, are treated with an alkaline solution, in particular at pH

11-14, especially 12-13. This treatment is followed by an oxidative chemical treatment. The alkaline treatment is used for (partial) solubilisation of the (poly)carbohydrates, resulting in a better access to the polyphenol protein complex, without oxidising agent being spent by oxidising the polysaccharides and other oxidisable, alkali-soluble 5 material. The polyphenol-protein complex is subsequently removed by typical oxidative chemical aids such as sodium hypochlorite, organic and inorganic peracids and the like.

The second embodiment uses a back-wash step. Since research has revealed that the polyphenol protein complex is directly attached through physical bonds to the membrane surface, surprisingly it is possible to target the polyphenol protein complex 10 directly using typical oxidative chemicals such as sodium hypochlorite, organic and inorganic peracids and the like. For cleaning using a back-wash, it is preferred to use a back-wash flux of between 0,5 and 100 l of cleaning solution per h per m² per h for a period of time between 1 and 100 min, depending on the degree of fouling of the membrane.

15 For both cleaning modes, the cleaning chemicals are used in a concentration of between 1 and 5000 ppm, especially between 30 and 1000 ppm. Direct oxidants, such as hydrogen peroxide, hypohalite and peracids, are preferably used in ranges from 200 to 2000 ppm, whereas metal catalysts are preferably used at levels from 1 to 50 ppm. Depending on the type of cleaning aid the pH may vary between 3 and 11. The cleaning 20 temperature may be between 4 and 80 °C, preferably between 15 and 60 °C, most preferably between 20 and 50 °C. When using direct oxidants, such as peracids and hypohalous acids (hypochlorite, hypobromite, etc.), an acid pH (below 7) was found to be more efficacious; most preferably, the pH is between 4 and 6. When using a transition metal catalyst together with a peroxide, a neutral to moderately alkaline pH is 25 preferably used, in particular between pH 7 and 11, most preferably between 8 and 10.

After the cleaning process, using one of the above described methods, the filters are preferably rinsed with water several times before use. It is not necessary to use a reducing agent after the oxidative treatment in the process of the invention.

30 The peracid described may be any peralkanoic acid such as peracetic acid, perpropionic acid, perlauric acid etc., a substituted alkanoic acid such as peroxytrifluoroacetic acid, an optionally substituted aromatic peracid such as perbenzoic acid or m-chloroperbenzoic acid, or an inorganic peracid such as persulphuric acid or permanganic

acid. The peracids may be formed in situ from a precursor such as the corresponding aldehyde, (carboxylic) acid, acid anhydride, ester or amide, e.g. tetra-acetyl-ethylene-diamine (TAED), with a suitable halogen-free oxidising agent, such as hydrogen peroxide or oxygen, either before the oxidation reaction or during the oxidation reaction, or with perborates or percarbonates or the like, in the presence of acylating agents such as TAED. The peracids and hypohalous acids may be used as such, or in the form of a suitable salt, especially an alkali metal salt. A suitable form of persulphuric acid is e.g. Oxone® (2KHSO₅.KHSO₄.K₂SO₄), which is commercially available.

The transition metal oxidator can be a combination of a transition metal, such as iron, manganese, chromium, cobalt or vanadium, with a hydroperoxide, such as t-butyl hydroperoxide or another alkyl hydroperoxide, a hypohalite, a peracid or, preferably hydrogen peroxide or oxygen. The preferred transition metals are iron and, especially, manganese. The transition metal is preferably in the form of a complex with a nitrogen-containing organic compound, preferably containing at least two nitrogen atoms (i.e. a polyamine) such as ethylenediamine, diethylenetriamine, triazacyclononane and their N-methylated analogues, bipyridyl and the like. The transition metal catalysed system was found to be particularly effective, both in the circular and in the back-flush mode. When using the circular mode, the alkaline pretreatment can even be dispensed with when using the transition metal system, especially when a somewhat higher cleaning temperature is used, e.g. between 40 and 80°C.

For the back-wash method, the preferred oxidising agents include peracids such as Oxone, transition metal complexes with hydrogen peroxide.

It was found surprisingly that treatment of membrane filters using either of the two described methods results in a cleaning performance which is equal to or better than that treatment with hypochlorite/bromide in combination with TEMPO as described in WO 97/45523. Also the amount of cleaning chemical necessary for cleaning the membranes can be considerably reduced compared to method of WO 97/45523, since the cleaning chemical is only used to remove the polyphenol protein complex. The limited use of the chemical aid also is beneficial for the stability of the membranes used. As an example, the amount of oxidising agent to be used for cleaning membrane filters according to either one of the processes of the invention is between 100 and 2500 mg of

oxidising agent (hypochlorite) per 1000 l of beer produced, whereas the process of WO 97/45523 requires about 4500 mg of hypochlorite and additional TEMPO per 1000 l of the same type of beer. Similar improvements can be achieved for filter membranes used in the production of fruit juices and the like.

5 The process of the invention may be used for cleaning filters used in food industry and in feed industry. Such equipment may especially be used in the production of dairy products, beer, wine, fruit juices (apple, pineapple, grape, grapefruit, orange, lemon, etc.), vegetable juices and other beverages and liquids used in food processing. Suitable examples of such equipment include pipes, tubes, capillaries, mixing devices
10 and, in particular, filters. The filter may be of any type, including polymer membranes wherein the polymer may be polyvinylpyrrolidone, polysulphone, polyether-sulphone and especially polyamides, and ceramic membranes made of e.g. silica, aluminium oxide etc.

The process of the invention may proceed by solubilisation of carbohydrates
15 and oxidation and/or solubilisation other high molecular weight biomolecules proteinaceous materials, polyphenolic compounds, in residues to be removed from the filters. Such cleaning procedures are preferably carried out by treating the equipment with an aqueous solution of the chemical aid. The process of the invention can be performed as a static process, i.e. batch-wise treatment of the equipment in a suitable
20 container containing the treatment liquid for a period of between several seconds and several hours, especially between 3 minutes and 1 hour. The process can also be a dynamic process, i.e. a process wherein a continuous or semi-continuous flow of the treatment liquid is passed over or through the equipment, e.g. at a rate of 5 ml to 10 l per minute, depending on the size of the equipment. After the cleaning sequence, the
25 equipment is rinsed with rinsing liquid, which can be water or a neutralising aqueous liquid or an organic solvent such as an alcohol solution, or a mixture or sequential combination thereof.

Example 1: Cleaning filters using the circular method

A filtration membrane (hollow tube containing 40 membrane hollow fibres, pore size 0.5 micron) with a total surface area of 0.035 m² (resembling the X-flow R-100 modules used in large scale facilities) was used for dead-end filtering beer. The virgin flux of the membrane was 70 ml/sec. The fouled membrane was then recycled with a sodium hydroxide solution at pH 13 for 30 min. Then, the membrane was recirculated at room temperature with 3 litre of an oxidant solution as described in table 1 for 45 minutes. The concentration of chemicals is given in ppm (w/w). The clean water flux after the cleaning treatment is also given in table 1.

10 *Table 1: Circular cleaning*

example	oxidant	concentration (ppm)	pH	clean water flux (ml/sec)
1.1	hypochlorite	2000	7	55
1.2	hypochlorite	2000	10	55
1.3	peroxydisulphate	2000	10	20
1.4	hydrogen peroxide	2000	10	35
1.5	Oxone *	2000	9	30

*: 2KHSO₅.KHSO₄.K₂SO₄

Example 2: Cleaning filters by back flush using various oxidants

A cleaned filtration membrane (clean water flux 70 ml/sec) as described in example 1 was used for dead-end filtering beer. The fouled membrane was then back-flushed at room temperature with 3 litre of an oxidant solution as described in table 2. The clean water flux after the cleaning treatment is also given in table 2.

Table 2: Back flush cleaning

example	oxidant	concentration (ppm)	pH	clean water flux (ml/sec)
2.1	oxone*	1000	9	30
2.2	oxone	1000	5	35
2.3	hypochlorite	2000	10	55
2.4	hypochlorite	2000	7	55
2.5	peroxydisulphate	2000	10	20
2.6	peroxydisulphate + Br	2000 + 100	10	25
2.7	peroxydisulphate	2000	7	20
2.8	hydrogen peroxide	2000	10	40
2.9	hydrogen peroxide	2000	7	40

*: 2KHSO₅.KHSO₄.K₂SO₄

Example 3: Cleaning filters by back flush using various oxidants and a metal catalyst

Example 3 was repeated using 2 litre of an oxidant solution at about 30°C as described in table 3. The clean water flux after the cleaning treatment is also given in table 3.

Table 3: Back flush cleaning

example	oxidant	concentration (ppm)	pH	time (min)	clean water flux (ml/sec)
3.1	Mn-TMTA** + H ₂ O ₂	5 + 16,500	9.3	30	66
3.2	Mn-TMTA** + H ₂ O ₂	5 + 3000	9.3	30	62
3.3	Mn-TMTA** + AcOOH	5 + 2500	8.5	30	51
				60	66
				90	72
3.4	Mn-TMTA** + hypochlorite	5 + 2000	9.5	30	74
3.5	hypochlorite	2000	5	30	62
				60	72

** TMTA: trimethyltriazonane

Example 4: Cleaning filters by back flush using various oxidants

Example 2 was repeated using 1 litre of an oxidant solution at 25-40°C as described in table 4. The clean water flux after the cleaning treatment is also given in table 4.

Table 4: Back flush cleaning

example	oxidant	concentra- tion (ppm)	pH	temper- ature (°C)	clean water flux (ml/sec)
4.1	chlorite + hypochlorite	1300 + 300	9-10	25	30
4.2	Mn-TMTA**+ H ₂ O ₂	5 + 10,000	9-10	40	75
4.3	Mn-TMTA** H ₂ O ₂	5 + 8000	9-10	40	75

5 ** TMTA: trimethyltriazonane

Claims

1. A process of cleaning a filter containing residues from filtering beverages, the residues containing water-insoluble proteins and/or polyphenols attached to the filter and polysaccharides, comprising contacting the protein and/or polyphenol containing residues with a solution containing an oxidising agent capable of oxidising proteins and/or polyphenols while minimising contact of the oxidising agent with the polysaccharides.
2. A process according to claim 1, wherein the oxidising agent is a peroxide compound or a hypohalous acid, and the oxidising agent is used in the presence of a transition metal.
3. A process according to claim 2, wherein the transition metal is manganese or iron.
4. A process according to claim 2 or 3, wherein the transition metal is complexed with a polyamine.
5. A process according to claim 2, wherein the oxidising agent is hydrogen peroxide.
6. A process according to claim 2, wherein the oxidising agent is a peracid.
7. A process according to claim 1, wherein the oxidising agent is a hypohalous acid, and the solution has a pH between 4 and 7.
8. A process according to any one of claims 1-7, wherein the filter, prior to contacting with the solution of the oxidising agent, is contacted with an alkaline solution.
9. A process according to claim 8, wherein the alkaline solution has a pH between 11 and 14.
10. A process according to any one of claims 1-7, wherein contacting with the solution of the oxidising agent is performed as a back-flush.
11. A process according to claim 10, wherein the back-flush is performed at a rate of 0.5 - 100 l of the solution per h per m² of filter surface.

12. A process of cleaning a filter containing residues from filtering beverages, the residues comprising water-insoluble proteins and/or polyphenols attached to the filter and polysaccharides, comprising contacting the protein and/or polyphenol containing residues with a solution containing an oxidising agent comprising a peroxide compound together with a transition metal complex.

INTERNATIONAL SEARCH REPORT

PCT/NL 03/00461

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D65/06 B01D65/02 C12H1/06 B01D41/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D C12H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 45523 A (LHS MICRO FILTRATIONS B V ;MOL MARTINUS NICOLAAS MARIA (NL); HEINE) 4 December 1997 (1997-12-04) cited in the application the whole document	1,2,12
Y	---	3-5,10, 11
X	DE 195 03 060 A (HENKEL ECOLAB & CO OGH) 8 August 1996 (1996-08-08) the whole document	1
X	US 4 740 308 A (AGAR RICHARD C ET AL) 26 April 1988 (1988-04-26) the whole document	1
Y	EP 0 733 594 A (TNO) 25 September 1996 (1996-09-25) column 1, line 44 -column 3, line 16	3-5
	---	-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

14 August 2003

Date of mailing of the international search report

27/08/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Martini, P

INTERNATIONAL SEARCH REPORT

PCT/NL J3/00461

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>PATENT ABSTRACTS OF JAPAN vol. 017, no. 055 (C-1023), 3 February 1993 (1993-02-03) -& JP 04 267933 A (FUJI PHOTO FILM CO LTD), 24 September 1992 (1992-09-24) abstract -& DATABASE WPI Derwent Publications Ltd., London, GB; AN 1992-368433 XP002215044 & JP 04 267933 A (FUJI PHOTO FILM CO LTD), 24 September 1992 (1992-09-24) abstract</p> <p>---</p>	10,11
A	<p>TRAGARDH G: "MEMBRANE CLEANING" DESALINATION, ELSEVIER SCIENTIFIC PUBLISHING CO, AMSTERDAM, NL, vol. 71, no. 3, 1 March 1989 (1989-03-01), pages 325-335, XP000087751 ISSN: 0011-9164 page 327 page 331</p> <p>-----</p>	1-12

INTERNATIONAL SEARCH REPORT

PCT/NL T3/00461

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 9745523	A	04-12-1997		NL 1003225 C2 AT 228560 T AU 717265 B2 AU 2915597 A BG 102972 A BR 9709282 A CN 1226922 A CZ 9803922 A3 DE 69717451 D1 DE 69717451 T2 DK 912701 T3 EP 1260576 A2 EP 0912701 A1 ES 2188942 T3 HU 9904021 A2 IL 127318 A JP 2000511218 T KR 2000016193 A WO 9745523 A1 NO 985602 A NZ 333071 A PT 912701 T RU 2197516 C2 SK 165798 A3 TR 9802544 T2 US 6274186 B1		03-12-1997 15-12-2002 23-03-2000 05-01-1998 30-09-1999 11-01-2000 25-08-1999 11-08-1999 09-01-2003 03-07-2003 24-03-2003 27-11-2002 06-05-1999 01-07-2003 28-03-2000 20-05-2001 29-08-2000 25-03-2000 04-12-1997 18-01-1999 29-07-1999 28-02-2003 27-01-2003 13-03-2000 22-03-1999 14-08-2001
DE 19503060	A	08-08-1996		DE 19503060 A1 AT 178500 T DE 59601608 D1 DK 808212 T3 WO 9623579 A1 EP 0808212 A1		08-08-1996 15-04-1999 12-05-1999 18-10-1999 08-08-1996 26-11-1997
US 4740308	A	26-04-1988		NONE		
EP 0733594	A	25-09-1996		NL 9500551 A EP 0733594 A1 US 5667690 A		01-11-1996 25-09-1996 16-09-1997
JP 04267933	A	24-09-1992		NONE		